

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

APPROV

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(b)(2).

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TITLE OF THE INVENTION (280 characters max.)

PLASTICIZED WATERBORNE POLYURETHANE DISPERSIONS AND
MANUFACTURING PROCESS

CORRESPONDENCE ADDRESS

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No
☐ Yes, the name of the U.S. Government agency and the Government contract number are:

Respectfully submitted,

SIGNATURE: Charles A. Crehore Date: July 20, 2000

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**CERTIFICATE OF MAILING BY "EXPRESS MAIL"
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PLASTICIZED WATERBORNE POLYURETHANE DISPERSIONS AND MANUFACTURING PROCESS

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FIELD OF THE INVENTION

This invention relates to waterborne polyurethane dispersions prepared using a plasticizer as a prepolymer diluent. Such dispersions have higher solids and produce articles having lower modulus than articles made from dispersions prepared using a prepolymer diluent such as N-methyl-2-pyrrolidone (NMP).

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BACKGROUND OF THE INVENTION

U.S. Patent No. 6,017,997 (incorporated herein by reference) relates to waterborne polyurethanes having film properties comparable to rubber. A prepolymer is formed by reacting (1) a polyisocyanate component; (2) an active hydrogen containing component, such as a polyol or a polyamide; and (3) a water-solubilizing compound having water-solubilizing groups to form an isocyanate terminated prepolymer. The prepolymer is (1) neutralized by reaction with a tertiary amine, (2) dispersed in water, and (3) then chain extended by reaction with a primary or secondary amine. N-methyl-2-pyrrolidone (NMP) may be used as a coalescing (film forming) agent, and also as a diluent to render the viscosity of the prepolymer low enough to process it

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readily. However, NMP reduces the solids of the dispersion and is undesirable as a volatile organic compound (VOC) from an environmental standpoint. Excess isocyanate may also be used as a diluent but will increase the modulus of polyurethane articles made from the dispersions. Such higher modulus is undesirable for producing a "rubbery" polymer.

U.S. Patent No. 4,306,998 relates to auxiliary agents and additives that are insoluble and not dispersible in water and are incorporated in oligo- and polyurethanes before the latter are dispersed in water. Plasticizers are among many such additives listed, but there is no suggestion that plasticizers replace diluents such as NMP. The desirability of solvent-free dispersions is mentioned, but solvents (acetone and NMP are among the compounds listed as solvents) generally are distilled off before the oligo- or polyurethane is dispersed or during or immediately after dispersion in order to obtain a solvent-free dispersion.

An improved polyurethane manufacturing process is desired that produces improved polyurethane dispersions having higher solids, lower modulus, and other improved properties compared to polyurethanes of the prior art.

SUMMARY OF THE INVENTION

Waterborne polyurethane dispersions are prepared using a plasticizer as a prepolymer diluent in order to wholly or partially replace prior art diluents such as N-2-methyl pyrrolidone (NMP). Such dispersions have higher solids and produce articles having lower modulus and other improved properties compared to articles made from dispersions prepared using the prior art prepolymer diluents.

The waterborne polyurethane dispersions are prepared by reacting (1) a polyisocyanate component; (2) an active hydrogen containing, high molecular weight component, such as a polyol or a polyamide; and (3) a water-solubilizing compound having water-solubilizing groups to form an isocyanate terminated prepolymer. The prepolymer subsequently is (1) neutralized by reaction with a tertiary amine, (2) dispersed in water, and then (3) chain extended by reaction with a primary and/or secondary amine. A plasticizer is introduced into the reaction mixture as a diluent at any time during prepolymer formation or before the prepolymer is dispersed in water. The plasticizer wholly or partially replaces other diluents or solvents.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to waterborne polyurethane dispersions prepared by reacting (1) a polyisocyanate component; (2) an active hydrogen

containing, high molecular weight component, such as a polyol or a polyamide; and (3) a water-solubilizing compound having water-solubilizing groups in order to form an isocyanate terminated prepolymer. The prepolymer subsequently is (1) neutralized by reaction with a tertiary amine, (2) dispersed in water, and (3) then chain extended by reaction with a primary and/or secondary amine. A plasticizer is introduced into the reaction mixture at any time during prepolymer formation or before the prepolymer is dispersed in water.

Suitable polyisocyanates have an average of about two or more isocyanate groups, preferably an average of about two to about four isocyanate groups and include aliphatic, cycloaliphatic, araliphatic, and aromatic polyisocyanates, used alone or in mixtures of two or more. Diisocyanates are more preferred.

Specific examples of suitable aliphatic polyisocyanates include alpha, omega-alkylene diisocyanates having from 5 to 20 carbon atoms, such as hexamethylene-1,6-diisocyanate, 1,12-dodocane diisocyanate, 2,2,4-trimethyl-hexamethylene diisocyanate, 2,4,4-trimethyl-hexamethylene diisocyanate, 2-methyl-1,5-pentamethylene diisocyanate, and the like. Preferred aliphatic polyisocyanates include hexamethylene-1,6-diisocyanate, 2,2,4-trimethyl-hexamethylene-diisocyanate, and 2,4,4-trimethyl-hexamethylene diisocyanate.

Specific examples of suitable cycloaliphatic polyisocyanates include dicyclohexylmethane diisocyanate, (commercially available as Desmodur™ W

from Bayer Corporation), isophorone diisocyanate, 1,4-cyclohexane diisocyanate, 1,3-bis(isocyanatomethyl) cyclohexane, and the like. Preferred cycloaliphatic polyisocyanates include dicyclohexylmethane diisocyanate and isophorone diisocyanate.

5 Specific examples of suitable aliphatic polyisocyanates include m-tetramethyl xylylene diisocyanate, p-tetramethyl xylylene diisocyanate, 1,4-xylylene diisocyanate, 1,3-xylylene diisocyanate, and the like. Preferred aliphatic polyisocyanates include tetramethyl xylylene diisocyanate.

10 Examples of suitable aromatic polyisocyanates include methane-bis(4-phenyl isocyanate), toluene diisocyanate, their isomers, and the like. Preferred aromatic polyisocyanates include toluene diisocyanate.

15 The preferred diisocyanate is an aliphatic diisocyanate. Isophorone diisocyanate (IPDI) and an isomer blend of 2,2,4- and 2,4,4-trimethyl hexamethylene diisocyanate (TMDI) are the aliphatic diisocyanates of choice for surgical gloves because of their inherent "softness" (in order to make low modulus films), lower prepolymer viscosity, and relatively high tensile strength capabilities.

20 Other polyisocyanates may be used in whole or in part substitution to attain similar properties, but will lessen certain polymer qualities. For example, tetramethyl xylylene diisocyanate (TMXDI) decreases tensile strength, and methylene bis-(4-cyclohexylisocyanate) (H₁₂MDI) and methylene bis-(4-

phenylisocyanate) (MDI) increase modulus. Toluene diisocyanate (TDI) works in the present invention if non-yellowing properties are not required.

The term "polyol" denotes any high molecular weight product, typically referred to as a long-chain polyol, which has an active hydrogen that can be reacted and includes materials having an average of about two or more hydroxyl groups per molecule. Such long-chain polyols which can be used in the present invention include higher polymeric polyols such as polyester polyols and polyether polyols, as well as polyhydroxy polyester amides, hydroxyl-containing polycaprolactones, hydroxyl-containing acrylic interpolymers, hydroxyl-containing epoxies, hydrophobic polyalkylene ether polyols, and the like, and mixtures thereof.

The polyester polyols are esterification products prepared by the reaction of organic polycarboxylic acids or their anhydrides with a stoichiometric excess of a polyol. Examples of suitable polyols for use in the reaction include polyglycol adipates, polyethylene terephthalate polyols, polycaprolactone polyols, orthophthalic polyols, sulfonated polyols, and the like, and mixtures thereof.

The polycarboxylic acids and polyols used in making the polyester polyols are typically aliphatic or aromatic dibasic acids and diols. The diols used in making the polyester polyols include alkylene glycols, e.g., ethylene glycol, butylene glycols, hexane diols, neopentyl glycol, and other glycols such

as bisphenol-A, cyclohexane diol, cyclohexane dimethanol, caprolactone diol, hydroxylated bisphenols, polyether glycols, and the like, and mixtures thereof. Preferred diols include ethylene glycol, butylene glycol, hexane diol, and neopentyl glycol, with ethylene glycol and butylene glycol being of particular use in making surgical gloves.

Suitable carboxylic acids used in making the polyester polyols include dicarboxylic acids and tricarboxylic acids, e.g., maleic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, azelaic acid, sebacic acid, chlorendic acid, 1,2,4-butane-tricarboxylic acid, phthalic acid, terephthalic acid, the isomers of phthalic acid, and the like, and mixtures thereof.

Preferably, the polyester polyol for making surgical gloves should be as non-crystalline as possible and in that regard should have a broad melting range and be liquid at 90° F. or lower. The average molecular weight for the polyester polyol should be at least 2400 to afford high elongation and low tensile modulus at a given elongation. The preferred molecular weight for the polyols and polyamides used in making surgical gloves is from about 2400 to about 5500 Daltons.

The preferred polyester polyol is a diol. Preferred polyester diols include hexane diol neopentyl glycol adipic acid polyester diol, e.g., 67-3000 HNA (Panolam Industries) and 67-1000 HNA (Panolam Industries); as well as propylene glycol maleic anyhydride adipic acid polyester diols, e.g., 50-

1000PMA (Panolam Industries); and hexane diol neopentyl glycol fumaric acid polyester diols, e.g., 67-500HNF (Panolam Industries). Other preferred polyester diols include Rucoflex® S1015-35 , S1040-35, and S-1040-110 (RUCO Polymer Corp.).

5 Polyether diols may be substituted in whole or in part for the polyester diols; however, larger amounts of polyether diols tend to lower tensile strength. Preferred polyethers include polypropylene glycol and copolymers of polyethylene glycol and polypropylene glycol. The use of the Acclaim® series such as Acclaim® 3201 (Arco Chemical), improved polyether diols with lower
10 monol contents, does not reduce tensile strength significantly as would conventional polyether diols. In addition, these polyether diols give significantly lower prepolymer viscosities, which allow easier manufacture of solvent-free, low-modulus polyurethanes.

Instead of a long-chain polyol, a long-chain amine may also be used in
15 the practice of this invention. Suitable amines include Jeffamine® D-2000 and D-4000, which are amine-terminated polypropylene glycols, differing only by molecular weight, and which are available from Huntsman Chemical Company. It is also recognized that other difunctional active hydrogen containing materials in a suitable molecular range (typically averaging about 2400 to about 5550
20 Daltons) may be suitable for this application.

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To enhance the water solubility, a water-solubilizing compound bearing a group that is water-soluble or can be made water-soluble is incorporated into the polymer chain. One particularly preferred water-solubilizing compound is 2,2-bis(hydroxymethyl) propionic acid (DMPA). Other suitable water-solubilizing compounds include the following: tartaric acid, dimethylol butanoic acid (DMBA), glycolic acid, thioglycolic acid, lactic acid, malic acid, dihydroxy malic acid, dihydroxy tartaric acid, and 2,6-dihydroxy benzoic acid.

Water-solubilizing groups are incorporated in the prepolymer in an inactive form in the water-solubilizing compound and subsequently activated by a salt-forming compound such as a tertiary amine as described more fully hereinafter. The water-solubilizing groups are hydrophilic or ionic groups whose presence in the polymer assists solubility or dispersability of the polymer in water and enhances the stability of polymer dispersions. Polyurethanes are generally hydrophobic and not water-dispersable.

The formation of the isocyanate terminated prepolymer may be achieved without the use of a catalyst. However, a catalyst is preferred in some instances. Examples of suitable catalysts include stannous octoate, dibutyl tin dilaurate, and tertiary amine compounds such as triethylamine and bis(dimethylaminoethyl) ether, morpholine compounds such as β,β' -dimorpholinodiethyl ether, bismuth carboxylates, zinc bismuth carboxylates, iron (III) chloride, potassium octoate, potassium acetate, and DABCO®

(bicycloamine). The preferred catalyst is FASCAT® 2003 from Elf Atochem North America. The amount of catalyst used is typically from about 10 to about 40 parts per million of the isocyanate terminated prepolymer.

The polyurethane is prepared in the presence of a plasticizer that acts as a diluent in order to render the viscosity of the polyurethane dispersion low enough to process it. The plasticizer can be added at any time during prepolymer preparation or before the prepolymer is dispersed in water, e.g., separately or as a mixture with one or more reaction components prior to prepolymer preparation.

Use of a plasticizer as a diluent serves a number of important functions. First, use of diluents (such as N-methyl-2-pyrrolidone (NMP) and the like) and solvents (such as acetone and the like) is avoided or reduced, together with attendant fire, pollution and toxicity hazards of such diluents and solvents. Furthermore, solids content of the final product is increased, since the plasticizer remains in the final product and does not require a burdensome product purification process. Moreover, intimate mixing of the plasticizer occurs, thereby avoiding or reducing problems that can occur with plasticizer addition any time after the prepolymer is dispersed in water, such as stratification and bleeding. (Stratification and bleeding can occur when a plasticizer is added following prepolymer dispersion in water; the plasticizer typically is not well mixed and separates from the composition.) Moreover,

addition of plasticizer during prepolymer formation or before prepolymer dispersion in water enhances polyurethane film formation during subsequent processing to form articles such as gloves, since the intimately mixed plasticizer allows easier coalescence. Moisture resistance of the polyurethanes of this invention also is enhanced, since the intimately mixed plasticizer is hydrophobic and tends to slow hydrolysis, especially of polyester-based polyurethanes.

Plasticizers are selected for use in this invention according to parameters such as compatibility with the particular polyurethane and desired properties of the final composition. For example, polyester plasticizers tend to be more compatible with polyester-based polyurethanes. Reactive plasticizers can be used that react with functionality of the ingredients. For example, epoxy groups may be present in reactive plasticizers that react with other components such as aminated and hydroxylated components respectively. Ethylenically unsaturated groups may be present in reactive plasticizers that react with components having ethylenic unsaturation. Plasticizers can also be selected to impart particular properties such as flame retardancy to the polyurethanes. The plasticizers typically are used for gloves in amounts from about 5 to about 25 wt.% based on prepolymer weight.

Suitable plasticizers include ester derivatives of such acids and anhydrides as adipic acid, azelaic acid, benzoic acid, citric acid, dimer acids, fumaric acid, isobutyric acid, isophthalic acid, lauric acid, linoleic acid, maleic

acid, maleic anhydride, melissic acid, myristic acid, oleic acid, palmitic acid, phosphoric acid, phthalic acid, ricinoleic acid, sebacic acid, stearic acid, succinic acid, 1,2-benzenedicarboxylic acid, and the like, and mixtures thereof. Also suitable are epoxidized oils, glycerol derivatives, paraffin derivatives, sulfonic acid derivatives, and the like, and mixtures thereof and with the aforesaid derivatives. Specific examples of such plasticizers include dicapryl adipate, dimethyl azelate, diethylene glycol dibenzoate and dipropylene glycol dibenzoate (such as the K-Flex® esters from Kalama Chemical), triethyl citrate, dibutyl fumarate, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, methyl laurate, methyl linoleate, di-n-butyl maleate, tricapryl trimellitate, isopropyl myristate, butyl oleate, methyl palmitate, tricresyl phosphate, diethyl phthalate, the n-butylbenzyl ester of o-phthalic acid, butyl ricinoleate, dimethyl sebacate, methyl stearate, diethyl succinate, the butyl phenylmethyl ester of 1,2-benzenedicarboxylic acid, epoxidized linseed oil, glycerol triacetate, chloroparaffins having about 40% to about 70% Cl, o,p-toluenesulfonamide, and mixtures thereof.

Examples of suitable reactive plasticizers include compositions and mixtures having ethylenic unsaturation, such as triallyl trimellitate (TATM), Stepanol PD-200LV (a mixture of (1) unsaturated oil and (2) polyester diol reaction product of o-phthalic acid and diethylene glycol from Stepan Company), and the like, and mixtures thereof. Other suitable reactive

plasticizers include epoxidized plasticizers, including certain monofunctional and polyfunctional glycidyl ethers such as Heloxy® Modifier 505 (polyglycidyl ether of castor oil) and Heloxy® Modifier 71 (dimer acid diglycidyl ether) from Shell Chemical Company, and the like, and mixtures thereof.

5 Examples of suitable flame retardant plasticizers include phosphorus-based plasticizers such as cyclic phosphates and phosphate esters, exemplified by Pliabrac TCP (tricresyl phosphate), Pliabrac TXP (trixylenyl phosphate), Antiblaze N (cyclic phosphate esters), Antiblaze TCP (tar acid, cresol, xylyl, phenol phosphates), and Antiblaze 524 (trixylyl phosphate) from Albright & 10 Wilson Americas; Firemaster BZ 54 (halogenated aryl esters) from Great Lakes Chemicals; and the like. Other examples of phosphorus-based plasticizers include chlorinated alkyl phosphate esters such as Antiblaze 100 (chloro alkyl diphosphate ester) from Albright & Wilson Americas; alkyl phosphates and phosphites such as tributyl phosphate and triisooctyl phosphite; and the like, and 15 mixtures thereof.

Even with use of a plasticizer as diluent, the prepolymer should be made in such a way as to minimize its resultant viscosity. In neat (no solvent) and solution polymers, viscosity is determined largely by the molecular weight of the polymer. To minimize the molecular weight of a finished prepolymer, an 20 NCO/OH ratio of about 2/1 should be used. In this way the diol portions are essentially endcapped by the diisocyanate species, leaving an isocyanate

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terminated prepolymer of relatively low viscosity. As the NCO/OH ratio of a prepolymer is reduced, the resultant viscosity increases dramatically. It is recognized that diluent-free materials can be made at below about 2/1 NCO/OH ratios, but they become more difficult to process, pump, stir, and the like. Also, higher temperatures will be needed to work with such a prepolymer, which increases the likelihood of undesirable side reactions.

As the NCO/OH ratio of a prepolymer is increased above about 2/1, the molecular weight will be limited as with the 2/1 ratio, but the excess diisocyanate will function as a diluent, further reducing viscosity. While this is a desired effect, raising the NCO/OH ratio above about 2/1 can also have negative effects. When isocyanate content of a polyurethane is increased, the hardness, or modulus of the polyurethane, along with the yield point, is increased. This is undesirable for producing a "rubbery" polymer. Also, when excess diisocyanate (obtained from using an NCO/OH ratio much greater than about 2/1) is introduced into a dispersion, and this dispersion is then extended with a primary (or secondary) amine, high molecular weight polyureas may be formed. These materials are not soluble, but by controlling the ratio in the range of closer to about 2/1, the results will be increasingly satisfactory. If an excess of isocyanate is used, the result may be gels or grittiness in a cast film, and sediment in the dispersion. This can lead to weakened films having a poor appearance. For these reasons, NCO/OH ratios of about 1.4/1 to about 2/1 are

preferred for making surgical gloves, and ratios of about 1.5/1 to about 1.8/1 are more preferred.

The acid content of the water-solubilizing compound is yet another consideration for producing a low viscosity prepolymer. Higher acid numbers will lead to higher viscosity, but there is also a minimum amount of acid needed to render a given polyurethane backbone dispersable. The preferred carboxyl containing diol in this invention is dimethylol propionic acid (DMPA). The preferred range of carboxyl containing diol or water-solubilizing compound for making surgical gloves is from about 2 wt.% to about 4 wt.% of the total prepolymer, i.e., excluding plasticizer. The amount used will approach 2 wt.% as the backbone becomes more hydrophilic, as with higher concentrations of polyether diol. As the backbone becomes more hydrophobic, as with polyester based systems, the acid content needed for dispersion will approach 3-4 wt.%.

Neutralization of the prepolymer having dependent carboxyl groups with the tertiary amine converts the carboxyl groups to carboxylate anions, thus having a solubilizing effect. Suitable tertiary amines which can be used to neutralize the prepolymer include triethyl amine (TEA), which is preferred for making surgical gloves, as well as dimethyl ethanolamine (DMEA), N-methyl morpholine, and mixtures thereof. It is recognized that primary or secondary amines may be used in place of tertiary amines, if they are sufficiently hindered to avoid interfering with the chain extension process.

As a chain extender, any inorganic or organic amine having an average of about 2 or more primary and/or secondary amine groups is suitable for use in the present invention. Suitable organic amines for use as a chain extender include diethylene triamine (DETA), ethylene diamine (EDA), meta-xylylenediamine (MXDA), aminoethyl ethanolamine (AEEA), and 2-methyl pentane diamine. Also suitable for practice in the present invention are propylene diamine, butylene diamine, hexamethylene diamine, cyclohexylene diamine, phenylene diamine, tolylene diamine, 3,3-dichlorobenzidene, 4,4'-methylene-bis(2-chloroaniline), 3,3-dichloro-4,4-diamino diphenylmethane, and mixtures thereof. Other suitable inorganic amines include ammonia, hydrazine, substituted hydrazines, and hydrazine reaction products. Hydrazine is preferred and is most preferably used as a solution in water.

A degree of branching of the polymer may be beneficial, but is not required to maintain a high tensile strength and improve resistance to creep -- that is, recovery to that of or near its original length after stretching. This degree of branching may be accomplished during the prepolymer step or the extension step. For branching during the extension step, the chain extender DETA is preferred, but other amines having an average of about two or more primary and/or secondary amine groups may also be used. For branching during the prepolymer step, it is preferred that trimethylol propane (TMP) and other polyols having an average of about two or more hydroxyl groups be used.

When used, the branching monomers may be present in amounts from about 0.5 wt.% to about 4 wt.% of the polymer backbone. Preferably the requisite degree of branching needed is obtained during the chain extension step rather than during the prepolymer step. Otherwise, the high viscosity of the prepolymer resulting from branching may result in more difficult handling during the extension step.

The plasticized waterborne polyurethanes of the present invention may be useful in making rubbery articles having lower modulus than articles made without said plasticizer. Such polyurethanes have substantial amounts of both urethane and urea linkages and can be customized in a variety of ways to make polymers and products suitable for a variety of applications. For example, it typically is desirable during the manufacture of rubber-like articles (such as surgical gloves and the like by a coagulation process) to produce very soft, strong films from a solvent-free polymer. The coagulation process is well known to those skilled in the art and typically stiffens the polymer substantially, i.e., increases the polymer modulus 50% or more. The compositions of the present invention have lower modulus than prior art polymers for such applications. Alternatively, reactive plasticizers can be used as described heretofore to replace the plasticizers at least partially in applications where lower modulus is not important or is not as important, such as in hard, non-rubbery coatings for nails, articles such as furniture, and the like.

Additives such as activators, curing agents, stabilizers such as Stabaxol P200 and IGEPAL CO630, colorants, pigments, neutralizing agents, coagulating agents such as calcium nitrate, coalescing agents such as di(propylene glycol) methyl ether (DPM), waxes, slip and release agents, antimicrobial agents, surfactants such as Pluronic F68-LF, metals, antioxidants, UV stabilizers, antiozonants, and the like, can optionally be added during the manufacture of the compositions of this invention or during subsequent processing into finished products. Additives may be used as appropriate in order to make articles (especially flexible articles, such as gloves), or to impregnate, saturate, spray or coat papers, non-woven materials, textiles, wood, metals, polymeric articles, and a variety of other substrates. Applications include gloves; papers and non-wovens; fibrous materials such as textiles (including application to upholstery, carpets, tents, awnings, clothing, and the like); films, sheets, composites, and other articles; inks and printing binders; flock and other adhesives; and personal care products such as cosmetics, hair sprays, and nail polish; and the like.

The following examples are presented for the purpose of illustrating the invention disclosed herein in greater detail. However, the examples are not to be construed as limiting the invention herein in any manner, the scope of the invention being defined by the appended claims.

EXAMPLES

Chemicals Used in Examples

AEEA = aminoethyl ethanolamine from Aldrich Chemical Co., Inc.

5 Antiblaze N = cyclic phosphate esters from Albright & Wilson Americas

Antiblaze TCP = tar acid, cresol, xylyl, phenol phosphates from Albright & Wilson Americas

10 Antiblaze 100 = chloro alkyl diphosphate ester from Albright & Wilson Americas

Antiblaze 524 = trixylyl phosphate from Albright & Wilson

DBA = dibutylamine from Air Products and Chemicals

15 DeeFo XHD-47J from Ultra Additives Inc.

Dehydran 1293 = modified polysiloxane from Henkel

20 Desmodur W = methylene bis(4-cyclohexyl isocyanate) from Bayer Corporation

DMEA = dimethylethanolamine from Aldrich Chemical Co., Inc.

DMPA = dimethylol propanoic acid from Geo Specialty Chemicals Inc.

25 DOWFAX 2A1 = disodium (dodecyl sulfophenoxy) benzenesulfonic acid from Dow Chemical

DPM = di(propylene glycol) methyl ether from Dow Chemical

30 Ethylenediamine from Aldrich Chemical Co., Inc.

FASCAT 2003 = 2-ethyl hexanoic acid and stannous octoate from Elf Atochem North America

35 Firemaster BZ 54 = halogenated aryl ester from Great Lakes Chemicals

HCl = hydrochloric acid from J.T. Baker

40 Hydrazine = 35 wt.% solution in water from Olin Chemicals

IGEPAL C0630 = branched nonylphenoxypoly(ethyleneoxy)ethanol

IPDI = isophorone diisocyanate from Bayer Corporation.

5

K-Flex® DE = diethylene glycol dibenzoate ester from Kalama Chemical.

K-Flex® DP = dipropylene glycol dibenzoate ester from Kalama Chemical

10

K-Flex® 500 = blend of K-Flex® DE and K-Flex® DP from Kalama Chemical

NMP = N-methyl-2-pyrrolidone from BASF

Pluronic F68-LF from BASF

15

PPG-1025 = polypropylene glycol (average MW = 1025) from Bayer Corporation

PPG-2025 = polypropylene glycol (average MW = 2025) from Bayer Corporation

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Santicizer 160 = 1,2-benzenedicarboxylic acid, butyl phenylmethyl ester; and o-phthalic acid, n-butyl benzyl ester from Solutia

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SLS = sodium lauryl sulfate

S1040-35 = polyester diol having a molecular weight of about 3000 from Ruco Polymer Corp.

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S1040-110 = polyester diol having a molecular weight of about 1000 from Ruco Polymer Corp.

Stabaxol P200 = aromatic polycarbodiimide from Rhein Chemie

35

STEPANOL PD-200LV = mixture of (1) unsaturated oil and (2) polyester diol reaction product of o-phthalic acid and diethylene glycol from Stepan Company

TATM = triallyl trimellitate from The CP Hall Company

40

TEA = triethylamine from Air Products and Chemicals

TMDI = approximately a 50/50 blend of 2,2,4- and 2,4,4-trimethylhexamethylene-1,6-diisocyanate from Creanova, Inc.

TMP = trimethylolpropane from Celanese

TMXDI = tetramethylxylylene diisocyanate from Cytec Industries, Inc.

50-1000PMA = polyester diol reaction product of propylene glycol, maleic anhydride, and adipic acid (average MW = 1000) from Panolam Industries

67-1000HNA = polyester diol reaction product of hexane diol, neopentyl glycol, and adipic acid (average MW = 1000) from Panolam Industries

67-3000HNA = polyester diol reaction product of hexane diol, neopentyl glycol, and adipic acid (average MW = 3000) from Panolam Industries

67-500HNF = polyester diol reaction product of hexane diol, neopentyl glycol, and fumaric acid (average MW = 500) from Panolam Industries

Test Methods

1. Tensile strength, modulus and % elongation testing for Examples 1-5:

A glove mold is dipped into a coagulant solution, which contains calcium nitrate at a concentration of from about 2 to about 25%. The coagulant solution may also contain surfactants, thickeners, fillers, and other materials well known to those skilled in the art. The glove mold then is dried from about 1 minute to about 10 minutes at temperatures from about 50° C to about 120° C, forming a thin layer of powder on the surface of the glove mold. The mold then is dipped into the plasticized polyurethane latex and withdrawn slowly, forming a firm, wet gel on the glove mold. The gel is dried for about 1 to about 20 minutes at about 30-120° C in order to drive off most of the water from the wet gel. The glove then is cured at about 140-160° C for a time of about 8 minutes to about 12

minutes. After curing, the glove is stripped off the mold and allowed to cool overnight. Tensile testing is run the following day, using dumbbells cut to 1.5" in length, and 0.188" at the center. The starting gauge length is 0.75" and the jaw speed of the pulls is 20" per minute. Room temperature is 20-25° C, and relative humidity is 30-80%.

2. Tensile strength, modulus, and % elongation testing for Examples 20-

22: Each of the plasticized polyurethane dispersions of Examples 20-22 was diluted with 4% propylene glycol as a coalescing agent and then was drawn down on Mylar® film made from polyethylene terephthalate. The Mylar® film was attached to the glass by wetting the glass with DI (deionized) water and then applying the Mylar® film to the glass with pressure using a squeegee on top with a little DI water spray underneath. If no air bubbles were seen through the Mylar® film, then the attachment was complete. The film then was washed with DI water and dried with lint-free paper. The polyurethane test film was prepared by using a 10 mil. draw down bar to apply the polyurethane dispersion to the Mylar® film. After casting the polyurethane test film, it was through-dried at ambient temperature in a dust-free box. The Mylar® film and polyurethane film cast on it then were dried at 300° F for 3 minutes in an oven. Samples were stored for 24 hours at 50% humidity and 72° F in a temperature-conditioned room to equilibrate before testing. The Mylar® film with dried polyurethane film on it then was cut into 1-inch wide strips. The dried

polyurethane film was removed from the Mylar® film. The following polyurethane film parameters were measured: width (in) =1.000; thickness (inch) = 0.0016 to 0.0037; and spec gauge length (inch) =1.000. ASTM D882-95a tensile testing was performed using an Instron to measure various properties such as tensile strength, % elongation, and 100% modulus at break using these machine parameters: sample rate (pts/sec) =10; and crosshead speed in/min) =2.

3. Cracking/Splitting: The gloves are produced as test method 1 above. A visual inspection is made and any cracking or splitting of the gloves is noted.

4. Isopropanol resistance: The gloves are produced as in test method 1 above. A finger on a finished glove is stretched by hand to about 200% elongation. Two drops of Sterillium® disinfectant/antimicrobial handrinse are applied to the stretched glove finger. Gloves are rated for tearing/breaking, weakening, or severe tackiness. Gloves rated "good" do not tear, and show little-no tackiness or weakening.

Example 1

Prepolymer Step

The following materials were charged to a reactor: 1979.64 grams (1.31 equivalent) S1040-35 and 26.65 grams (0.05 equivalent) S1040-110; then with mixing, 484.04 grams (4.61 equivalent) TMDI and 62.19 grams (0.56

equivalent) IPDI were charged. Heat was applied to the batch to bring the temperature to over 190° F. After 2 hours, 87.48 grams (1.31 equivalent) DMPA was added, and the batch was held at over 190° F for approximately an additional 2 hours. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl, and was found to be 3.56%. Next, 660 grams (to a total of 20 wt.% plasticizer in the prepolymer) Santicizer 160 was added to the batch, and the batch then was allowed to cool to 173° F. 72.23 grams TEA was charged to the batch and was allowed to mix for about 10 minutes.

Extension Step

A portion (3066g) of this completed, neutralized prepolymer then was charged slowly, with mixing, into 2941g water (at 80° F), which contained 30.00 grams Pluronic F68-LF surfactant, over the course of about 25 minutes, thus forming an NCO-terminated prepolymer dispersion. To this dispersion, 122.4 grams was added of a 50/50 mixture of Stabaxol P200 and water. Chain extension was accomplished by adding 21.18 grams of a 50/50 blend of AEEA and water, and then 55.83 grams of 35 wt.% hydrazine solution.

Example 2

Prepolymer Step

The following materials were charged to a reactor: 2227.09 grams (1.47 equivalent) S1040-35 and 29.98 grams (0.06 equivalent) S1040-110; then with

mixing, 544.54 grams TMDI (5.19 equivalent); and 69.97 grams of IPDI (0.63 equivalent). Heat was applied to the batch to bring the temperature to over 190° F. After about 2 hours, 330 grams Santicizer 160 (to 10% total plasticizer in the prepolymer) and 98.42 grams DMPA (1.47 equivalent) were added with mixing, and the prepolymer was allowed to react for approximately 2 additional hours at over 190° F. The % NCO remaining then was measured, and was found to be 3.36%. The batch was cooled to 185° F. 81.5 grams TEA was charged to the batch and was allowed to mix for about 10 minutes.

Extension Step

A portion (3074 grams) of this completed, neutralized prepolymer was then charged slowly into 2828 grams water (at 79° F), which contained 15 grams Pluronic F68-LF surfactant, over the course of about 40 minutes, thus forming an NCO terminated prepolymer dispersion. Then 5.99 grams DeeFo XHD-47J defoamer was added to the dispersion, followed by 76.8 grams of 35 wt.% hydrazine solution (for chain extension), and 149.85 grams of an 80/20 mixture of water/Stabaxol P200.

Example 3

Prepolymer Step

The following materials were charged to a reactor: 2211.24 grams (1.46 equivalent) S1040-35 and 29.76 grams (0.06 equivalent) S1040-110; then with

mixing, 515.66 grams (4.91 equivalent) TMDI and 49.62 grams (0.45 equivalent) IPDI. Heat was applied to the batch to bring the temperature to over 190° F. After about 2 hours, 97.72 grams (1.46 equivalent) DMPA and 198 grams Santicizer 160 were added with mixing, and the prepolymer was allowed to react for approximately 2 additional hours at over 190° F. The % NCO remaining then was measured and found to be 2.82%. The batch was cooled to 178° F. TEA (80.93 grams) was charged to the batch and was allowed to mix for about 10 minutes.

Extension Step

A portion (3074 grams) of this completed, neutralized prepolymer then was charged slowly into 2848 grams water (at 76° F), which contained 30 grams Pluronic F68-LF surfactant, over the course of about 40 minutes, thus forming an NCO terminated prepolymer dispersion. About halfway through the dispersion, 6.01 grams DeeFo XHD-47J defoamer was added. After about 40 minutes mixing, 60.57 grams 35 wt.% hydrazine solution was added slowly to the dispersion (for chain extension). Over the course of the hydrazine extension, 782 additional grams of water were added to the dispersion. After four days, 150.3 grams of an 80/20 water/Stabaxol P200 mixture was added to the dispersion.

Example 4

Prepolymer Step

The following materials were charged to a reactor: 1962.7 grams (1.29 equivalent) S1040-35; then with mixing, 431.7 grams (4.11 equivalent) TMDI and 42.3 grams (0.38 equivalent) of IPDI. Heat was applied to the batch to bring the temperature to over 190° F. After about 2 hours, 243 grams Santicizer 160 and 83.2 grams DMPA (1.24 equivalent) were added with mixing, and the prepolymer was allowed to react for approximately 2-½ hours at over 190° F. An additional 237 grams of Santicizer 160 was then added to the prepolymer. The % NCO remaining then was measured and found to be 2.24%. The batch was cooled to 190° F. TEA (75.79 grams) was charged to the batch and allowed to mix for about 10 minutes.

Extension Step

A portion (2762 grams) of this completed, neutralized prepolymer was then charged slowly into 3261 grams of water (at 81° F), which contained 27 grams Pluronic F68-LF surfactant, over the course of about 24 minutes, thus forming an NCO terminated prepolymer dispersion. After mixing the dispersion about 50 minutes, 40.68 grams of 35 wt.% hydrazine solution was slowly added (for chain extension). About 295 grams of water was added after chain extension.

Example 5

Prepolymer Step

The following materials were charged to a reactor; 2004.6 grams (1.22 equivalent) 67-3000HNA and 90 grams (0.20 equivalent) 67-1000HNA; then with mixing, 611.5 grams (5.5 equivalent) IPDI was charged. Heat was applied to bring the temperature to over 200° F. After about 2 hours, 247.5 grams Santicizer 160 plasticizer and 98.8 grams (1.47 equivalent) DMPA were added, and the batch was held at over 195° F for about 90 minutes. An additional 247.5 grams Santicizer 160 was then added to the prepolymer batch. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl, and was found to be 3.28%. The prepolymer was then cooled to 172° F. 81.8 grams of TEA was charged to the batch and allowed to mix about 10 minutes.

Extension Step

A portion (3075 grams) of this completed, neutralized prepolymer was then charged slowly into 3086 grams of water (at 72° F), which contained 30 grams Pluronic F68-LF surfactant, over the course of about 25 minutes, thus forming an NCO terminated prepolymer dispersion. The dispersion was mixed for about 25 minutes, and then 81 grams of 35 wt.% hydrazine was added slowly, followed by 6.37 grams DeeFo XHD-47J defoamer.

Table 1 sets forth test data for Examples 1 to 4. In this table, "Plasticizer (wt.%) " is calculated based on the amount of plasticizer blended in the

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Table 1

Polymer	Example 1	Example 2	Example 3	Example 4
Coagulant Concentration (Ca(NO ₃) ₂ as wt.% of dispersion)	5%	5%	10%	6%
Cure Time 1 (minutes)	20	15	15	11
Cure Temperature (° F)	220	275	275	275-300
Cracking/Splitting	yes	yes	no	no
IPA (isopropanol) Resistance	fair	good	good	good
Plasticizer on Prepolymer (wt.%)	20	10	12	16
Polyester Soft Segment (wt.%)	76	76	77.17	77.88
100% Modulus (psi)	318	449	374	336
500% Modulus (psi)	981	1565	1173	777
Tensile Strength (psi)	1756	2318	2162	3023
Elongation (%)	633	576	626	757

Example 6

5 Prepolymer Step

The following materials were charged to a reactor: 236.82 grams (0.2309 equivalent) PPG-2025 and 218.70 grams (0.4187 equivalent) PPG-1025. The mixer then was turned on, and 219.99 grams (1.979 equivalent) of IPDI was added to the reactor, followed by 24.48 grams (0.3654 equivalent) DMPA and

0.050 gram of FASCAT 2003 catalyst. At this point, batch temperature was raised to over 190° F. The resultant mixture was allowed to react for two hours at 190-210° F with nitrogen purge and good stirring. The % NCO remaining was then measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 160° F, and 36.84 grams of Santicizer 160 was charged to the reactor. The mixture was stirred at 160° F for 10 minutes, and the prepolymer temperature was lowered to 150° F. Then 19.97 grams of TEA was added to the reactor and stirred for 15 minutes. The temperature of the finished prepolymer was lowered to 140° F for chain extension.

Extension Step

378.41 grams of finished prepolymer was charged slowly to a vessel containing 565.01 grams water at 70° F over 8.0 minutes and allow to mix for 15 minutes. Chain extension was then accomplished by slowly charging 20.88 grams 35 wt.% hydrazine solution over an 8 minute period. After the hydrazine solution was charged, mixing was continued for 30 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 7

Prepolymer Step

The following materials were charged to a reactor: 281.31 grams (0.2843 equivalent) PPG-2025 and 239.38 grams (0.4583 equivalent) PPG-1025. The mixer then was turned on, and 251.43 grams (2.262 equivalent) of IPDI was added to the reactor, followed by 27.98 grams (0.04176 equivalent) (DMPA and 0.0150 gram FASCAT 2003 catalyst. At this point, the batch temperature was raised to over 190° F. The resultant mixture was allowed to react for two hours at 190-210° F with nitrogen purge and good stirring. The % NCO remaining was then measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 190° F, and 600.00 grams of prepolymer was transferred into a new reactor, followed by charging 205.97 grams of Firemaster BZ 54 to the reactor. The mixture was stirred at 190° F for 20 minutes, and the prepolymer temperature was lowered to 145° F. Then 17.11 grams of TEA was added into the reactor, and it was stirred for 20 minutes. The temperature of the finished prepolymer was lowered to 140° F for chain extension.

Extension Step

190.00 grams of finished prepolymer were slowly charged to a vessel containing 290.81 grams water at 70° F and 53.48 grams 45% Dowfax 2A1 over an 8.0 minute period and allowed to continue mixing for 10 minutes. Chain

extension then was accomplished by slowly charging 7.09 grams 35 wt.% hydrazine solution over an 8 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

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Example 8

Prepolymer Step

The finished prepolymer of Example 8 was also chain extended as shown below.

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Extension Step

190.00 grams of finished prepolymer was charged slowly to a vessel containing 264.26 grams water at 70° F and 80.20 grams 30% SLS over an 8.0 minute period and allowed to mix for 10 minutes. Chain extension then was accomplished by slowly charging 7.09 grams 35 wt.% hydrazine solution over an 8 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

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Example 9

Prepolymer Step

5 The following materials were charged to a reactor: 281.31 grams (0.2843 equivalent) PPG-2025 and 239.38 grams (0.4583 equivalent) PPG-1025. The mixer then was turned on, and 251.43 grams (2.262 equivalent) IPDI was added to the reactor, followed by 27.98 grams (0.04176 equivalent) DMPA and 0.0150 gram of FASCAT 2003 catalyst. At this point the batch temperature was raised to over 190° F. The resultant mixture was allowed to react for two hours at 190-210° F with nitrogen purge and good stirring. The % NCO remaining was then measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 190° F, and 200.00 grams of prepolymer was transferred into a new reactor, followed by charging 68.66 grams of Antiblaze TCP to the reactor. The mixture was stirred at 190° F for 20 minutes, and the prepolymer temperature was lowered to 145° F. Then 5.71 grams of TEA was added to the reactor and stirred for 20 minutes. The temperature of the finished prepolymer was lowered to 140° F for chain extension.

Extension Step

20 120.00 grams of finished prepolymer was charged slowly to a vessel containing 202.24 grams water at 70° F and 15.20 grams IGEPAL CO630 over an 8.0 minute period and allowed to mix for 10 minutes. Chain extension then was accomplished by slowly charging 7.09 grams 35 wt.% hydrazine solution

over an 8 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

5 **Example 10**

Prepolymer Step

The finished prepolymer of Example 8 was also chain extended as shown below.

Extension Step

10 120.00 grams of finished prepolymer was charged slowly to a vessel containing 202.24 grams water at 70° F and 33.77 grams 45% DOWFAX 2A1 over an 8.0 minute period and allowed to continue mixing for 10 minutes. Chain extension then was accomplished by slowly charging 7.09 grams 35 wt.% hydrazine solution over an 8 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

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Example 11

Prepolymer Step

20 The following materials were charged to a reactor: 281.31 grams (0.2843 equivalent) PPG-2025 and 239.38 grams (0.4583 equivalent) PPG-1025. The

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mixer then was turned on, and 251.43 grams (2.262 equivalent) IPDI was added to the reactor, followed by 27.98 grams (0.04176 equivalent) DMPA and 0.0150 gram FASCAT 2003 catalyst. At this point the batch temperature was raised to over 190° F. The resultant mixture was allowed to react for two hours at 190-210° F with nitrogen purge and good stirring. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 180° F, and 400.00 grams of prepolymer was transferred into a new reactor, followed by charging 137.31 grams of Antiblaze into the reactor. The mixture was stirred at 190° F for 20 minutes, and the prepolymer temperature was lowered to 145° F. Then 11.41 grams of TEA was added to the reactor, and it was stirred for 20 minutes. The temperature of the finished prepolymer was lowered to 140° F for chain extension.

Extension Step

240.00 grams of finished prepolymer was slowly charged to a vessel containing 404.39 grams water at 70° F and 30.45 grams IGEPAL CO630 over a 10.0 minute period and allowed to mix for 10 minutes. Chain extension then was accomplished by slowly charging 10.27 grams 35 wt.% hydrazine solution over a 10 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 12

Prepolymer Step

The finished prepolymer of Example 8 was also chain extended as shown below.

5 Extension Step

240.00 grams of finished prepolymer was charged slowly to a vessel containing 426.39 grams water at 70° F and 30.45 grams 45% DOWFAX 2A1 over a 10.0 minute period and allowed to continue mixing for 10 minutes. Chain extension then was accomplished by slowly charging 10.27 grams of 35 wt.% hydrazine solution over an 8 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 13

15 Prepolymer Step

The following materials were charged to a reactor: 175.82 grams (0.1777 equivalent) PPG-2025 and 149.55 grams (0.2863 equivalent) PPG-1025. The mixer then was turned on, and 157.14 grams (1.4138 equivalent) IPDI was added to the reactor, followed by 17.49 grams (0.2610 equivalent) DMPA and 0.0150 gram FASCAT 2003 catalyst. At this point the batch temperature was raised to over 190° F. The resultant mixture was allowed to react for two hours

at 190-210° F with nitrogen purge and good stirring. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 165° F, and 400.00 grams of prepolymer was transferred into a new reactor, followed by charging 207.21 grams of Antiblaze 100 to the reactor. The mixture was stirred at 165° F for 10 minutes, and the prepolymer temperature was lowered to 140° F. Then 14.26 grams of TEA was added to the reactor, and it was stirred for 20 minutes. The temperature of the finished prepolymer was lowered to 140° F for chain extension.

Extension Step

330.00 grams of finished prepolymer was slowly charged to a vessel containing 511.98 grams water at 70° F and 18.63 grams IGEPAL CO630 over a 10.0 minute period and allowed to continue mixing for 10 minutes. Chain extension then was accomplished by slowly charging 13.17 grams 35 wt.% hydrazine solution over a 10 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 14

Prepolymer Step

The following materials were charged to a reactor: 175.82 grams (0.1777 equivalent) PPG-2025 and 149.55 grams (0.2863 equivalent) PPG-1025. The mixer then was turned on, and 157.14 grams (1.4138 equivalent) of IPDI was added to the reactor, followed by 17.49 grams (0.2610 equivalent) DMPA and 0.0150 gram of FASCAT 2003 catalyst. At this point, the batch temperature was raised to over 190° F. The resultant mixture was allowed to react for two hours at 190-210° F with nitrogen purge and good stirring. The % NCO remaining was then measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 195° F, followed by charging 207.21 grams of Antiblaze 524 to the reactor. The mixture was stirred at 165° F for 10 minutes, and the prepolymer temperature was lowered to 140° F. Then 14.26 grams of TEA was added to the reactor, and it was stirred for 20 minutes. The temperature of the finished prepolymer was lowered to 140° F for chain extension.

Extension Step

330.00 grams of finished prepolymer was charged slowly to a vessel containing 512.13 grams water at 70° F and 12.55 grams IGEPAL CO630 over a 10.0 minute period and allowed to mix for 10 minutes. Chain extension then was accomplished by slowly charging 13.67 grams 35 wt.% hydrazine solution

over a 10 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

5 **Example 15**

Prepolymer Step

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10 The following materials were charged to a reactor: 175.82 grams (0.1777 equivalent) PPG-2025 and 149.55 grams (0.2863 equivalent) PPG-1025. The mixer then was turned on, and 157.14 grams (1.4138 equivalent) of IPDI was added to the reactor, followed by 17.49 grams (0.2610 equivalent) DMPA and 0.0150 gram FASCAT 2003 catalyst. At this point the batch temperature was raised to over 190° F. The resultant mixture was allowed to react for two hours at 190-210° F with nitrogen purge and good stirring. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl. The finished

15 prepolymer was cooled to 195° F, followed by charging 207.21 grams of Antiblaze TXP to the reactor. The mixture was stirred at 165° F for 10 minutes, and the prepolymer temperature was lowered to 140° F. Then 14.26 grams of TEA was added to the reactor, and it was stirred for 20 minutes. The temperature of the finished prepolymer was lowered to 140° F for chain

20 extension.

Extension Step

330.00 grams of finished prepolymer was charged slowly to a vessel containing 512.13 grams water at 70° F and 12.55 grams IGEPAL CO630 over a 10.0 minute period and allowed to continue mixing for 10 minutes. Chain extension then was accomplished by slowly charging 13.67 grams 35 wt.% hydrazine solution over a 10 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 16

Prepolymer Step

The following materials were charged to a reactor: 2397.40 grams (1.4615 equivalent) 67-3000HNA and 125.25 grams (1.8694 equivalent) DMPA. The mixer then was turned on, and 664.00 grams (5.4382 equivalent) of TMXDI was added to the reactor, followed by 113.34 grams (1.0197 equivalent) IPDI. At this point the batch temperature was raised to over 200° F. The resultant mixture was allowed to react for 90 minutes at 215-225° F with nitrogen purge and good stirring. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 180° F, and 1650 grams prepolymer was transferred to a new reactor, followed by charging 426.69 grams of Santicizer 160 to the reactor. The mixture was stirred at 180°

F for 20 minutes, and the prepolymer temperature was lowered to 150° F. Then 56.75 grams of TEA was added into the reactor, and it was stirred for 15 minutes. The temperature of the finished prepolymer was lowered to 150° F for chain extension.

5 Extension Step

1900.00 grams of finished prepolymer was charged slowly to a vessel containing 2484.82 grams water at 70° F and 68.69 grams IGEPAL CO630 over a period of 12.0 minutes and allowed to continue mixing for 10 minutes. Chain extension then was accomplished by slowly charging 60.02 grams 35 wt.% hydrazine solution over a 12 minute period. After the hydrazine solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 17

15 Prepolymer Step

The following materials were charged to a reactor: 369.26 grams (1.437 equivalent) 67-500HNA and 660.30 grams (2.329 equivalent) STEPANOL PD-200LV. The mixer then was turned on, and 1455.87 grams (11.10 equivalent) of Desmodur W was added to the reactor. The mixture was allowed to exotherm to 230-240° F for 15 minutes and then cooled to 215-220° F. Then 23.34 grams TMP (0.5225 equivalent) and 0.15 gram FASCAT 2003 catalyst

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were charged to the reactor. The reactants were stirred for 15 minutes and cooled to 210° F. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl. 131.25 grams (1.959 equivalent) DMPA and 659.97 grams NMP, followed by 0.20 gram of FASCAT 2003 catalyst, were charged to the reactor. The resultant mixture was allowed to react for 60 minutes at 210° F with nitrogen purge and good stirring. The % of NCO remaining then was measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 165° F, and 1500.00 grams prepolymer was transfer separated for the following step. 60.00 grams of TATM was charged to the reactor. The mixture was stirred at 160° F for 20 minutes, and the prepolymer temperature was lowered to 145° F. Then 42.35 grams TEA was added to the reactor, and it was stirred for 10 minutes. The temperature of the finished prepolymer was lowered to 140° F for chain extension.

Extension Step

15 1500.00 grams of finished prepolymer was charged slowly to a vessel containing 1849.86 grams water at 70° F, 181.21 grams DPM and 1.81 grams Dehydran 1293 over a 20.0 minute period and allowed to continue mixing for 15 minutes. Chain extension then was accomplished by slowly charging a blend containing 47.85 grams 35 wt.% hydrazine solution, 21.69 grams ethylene diamine, and 21.69 grams water over a 25 minute period. After the blended solution was charged, mixing was continued for 30 minutes to complete the

chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 18

5 Prepolymer Step

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The following materials were charged to a reactor: 107.96 grams (0.420 equivalent) 67-500HNA and 49.71 grams (0.09853 equivalent) 50-1000PMA. The mixer then was turned on and 222.96 grams (1.70 equivalent) of Desmodur W was added to the reactor. The mixture was allowed to exotherm to 230-240° F for 15 minutes and then cooled to 215-220° F. Then 3.574 grams TMP (0.080 equivalent) and 0.015 gram FASCAT 2003 catalyst were charged. The reactants were stirred for 15 minutes and cooled to 210° F. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl. 20.10 grams (0.300 equivalent) DMPA and 101.08 grams NMP followed by 0.030 gram of FASCAT 2003 catalyst were charged to the reactor. The resultant mixture was allowed to react for 60 minutes at 210° F with nitrogen purge and good stirring. The percent of NCO remaining was then measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 145° F, and 256.04 grams of prepolymer was transferred into a new reactor. 20.53 grams of TATM was charged to the reactor. The mixture was stirred at 145° F for 5 minutes, and the prepolymer temperature was lowered to 145° F. Then

14.27grams of TEA was added to the reactor, and it was stirred for 10 minutes. The temperature of the finished prepolymer was adjusted to 145° F for chain extension.

Extension Step

5 200.00 grams of finished prepolymer was charged slowly to a vessel containing 374.40 grams water at 70° F, 29.45 grams DPM and 0.29 grams of Dehydran 1293 over a 7.0 minute period and allowed to mix for 10 minutes. Chain extension then was accomplished by slowly charging a blend containing 7.14 grams 35 wt.% hydrazine solution, 3.67 grams ethylene diamine, and 3.67 10 grams water over an 8 minute period. After the blended solution was charged, mixing was continued for 10 minutes to complete the chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 19

15 Prepolymer Step

 The following material was charged to a reactor: 251.05 grams (0.9778 equivalent) 67-500HNF. The mixer then was turned on and 351.49 grams (2.680 equivalent) of Desmodur W was added to the reactor. The mixture was allowed to exotherm to 230-240° F for 15 minutes and then cooled to 215-220° 20 F. Then 5.64 grams TMP (0.126 equivalent) and 0.03 gram FASCAT 2003 catalyst were charged. The reactants were stirred for 15 minutes and cooled to

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210° F. The % NCO remaining then was measured using a titration with (DBA and 1.0M HCl. 31.70 grams (0.473 equivalent) DMPA and 160 grams NMP, followed by 0.040 gram of FASCAT 2003 catalyst were charged to the reactor. The resultant mixture was allowed to react for 60 min at 210° F with nitrogen purge and good stirring. The % NCO remaining then was measured using a titration with DBA and 1.0M HCl. The finished prepolymer was cooled to 175° F, and 400.00 grams of prepolymer was transferred into a new reactor. 53.00 grams of TATM was charged to the reactor. The mixture was stirred at 175° F for 10 minutes, and the prepolymer temperature was lowered to 165° F. Then 11.25 grams of TEA was added to the reactor, and it was stirred for 10 minutes. The temperature of the finished prepolymer was adjusted to 160° F for chain extension.

Extension Step

330.00 grams of finished prepolymer was charged slowly to a vessel containing 448.21 grams water at 70° F, 39.74 grams DPM and 0.40 grams of Dehydran 1293 over a period of 8.0 minutes and allowed to continue mixing for 10 minutes. Chain extension then was accomplished by slowly charging a blend containing 8.68 grams 35 wt.% hydrazine solution, 3.94 grams ethylene diamine, and 3.94 grams water over an 8 minute period. After the blended solution was charged, mixing was continued for 20 minutes to complete the

chain extension. The result was a polymer that could be used or stored at ambient temperature.

Example 20

5 Prepolymer Step

10 NCO-terminated prepolymer was prepared in the prepolymer step. A one-gallon reactor was equipped with a mechanical stirrer, thermometer and nitrogen inlet. The reactor was charged with 0.45 equivalent of 67-1000 HNA, 1.5 equivalents of Desmodur W, and 0.5 equivalent of TMXDI, and then heated to 155° F. After 10 minutes of mixing at 155° F, 0.55 equivalent of acid DMPA was added to the mixture with good mixing, followed by three drops of FASCAT® 2003 catalyst. The resultant mixture was allowed to react for about two hours at 220° F. Then 10% of K-Flex® DP based on prepolymer weight was charged as diluent and mixed another 30 minutes at this temperature. The unreacted % NCO of the prepolymer was then determined by withdrawing a known amount of sample from reactor and titrating against DBA, followed by 1.0M HCl. The reaction mixture then was allowed to cool to 165° F. Prepolymer was neutralized by mixing thoroughly with 1.01 equivalents of TEA at about 160° F. The Brookfield viscosity of the extended polymer was measured as 1995 mPa.s at 161° F.

20

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Extension Step

Dispersion was carried out by charging 1150 grams of neutralized prepolymer into a vessel containing 2285.4 grams of water at 60° F with rapid mixing. Chain extension was carried out with slow addition of 35 wt.% diluted hydrazine (0.85 equivalent) for 15 to 30 minutes to obtain a dispersion from which a polyurethane could be made having lower modulus than if K-Flex® DP had not been employed as a plasticizer. Solids =32 wt.%; Viscosity = 12.5 mPa.s; and pH = 7.25.

Example 21

Prepolymer Step

Example 20 was repeated with 10% diethylene glycol dibenzoate ester (K-Flex® DE) as diluent. A slightly high viscosity neutralized prepolymer was obtained (30,000 mPa.s at 160° F).

Extension Step

The extension procedure was followed as mentioned before to obtain a dispersion from which a polyurethane could be made having lower modulus than if K-Flex® DE had not been employed as a plasticizer. Solids = 32 wt.%; Viscosity = 22.5 mPa.s; and pH = 7.56.

Example 22

Prepolymer Step

Example 20 was repeated with 10% K-Flex® 500, which is a blend of K-Flex® DE and K-Flex® DP, as diluent. The prepolymer was neutralized by mixing thoroughly with 1.01 equivalents of DMEA at about 160° F. The Brookfield viscosity of neutralized prepolymer was 15,400 mPa.s at 160° F.

Extension Step

A dispersion was made by charging 1260 grams of neutralized prepolymer into a vessel containing 2293.74 grams of water at 60° F with rapid mixing. Chain extension was completed with slow addition of 35 wt.% diluted hydrazine (0.85 equivalent) for 15 to 30 minutes to obtain a dispersion from which a polyurethane could be made having lower modulus than if K-Flex® 500 had not been employed as a plasticizer. Solids = 36.1 wt.%; Viscosity = 47.5 mPa.s; and pH = 8.62.

Tensile strength, % elongation and 100% modulus test results for Examples 20-22 are reported in Table 2. The compositions of Examples 20-22 (which have higher modulus than Examples 1-4) are useful in non-glove applications such as personal care products.

Table 2

	Example 20	Example 21	Example 22
100% modulus (psi)	3021	3202	3414
Tensile at max load (psi)	4461	5075	3965
Elongation at break (%)	255.7	283.9	201

5 While in accordance with the patent statutes the best mode and preferred embodiment has been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

CLAIMS

1. A process comprising:

(a) mixing (1) a polyisocyanate component, (2) an active hydrogen containing, high molecular weight component, and (3) a water-solubilizing compound having water-solubilizing groups;

(b) reacting the mixture to form an isocyanate terminated prepolymer; and

(c) subsequently (1) neutralizing said prepolymer by reaction with a tertiary amine, (2) dispersing the neutralized prepolymer in water, and (3) chain extending the neutralized, dispersed prepolymer by reaction with a primary and/or secondary amine;

wherein a plasticizer is introduced into the reaction mixture as a diluent at any time during prepolymer formation or before said prepolymer is dispersed in water, and said plasticizer wholly or partially replaces other diluents or solvents.

2. A composition prepared by a process comprising:

(a) mixing (1) a polyisocyanate component, (2) an active hydrogen containing, high molecular weight component, and (3) a water-solubilizing compound having water-solubilizing groups;

(b) reacting the mixture to form an isocyanate terminated prepolymer;
and

(c) subsequently (1) neutralizing said prepolymer by reaction with a
tertiary amine, (2) dispersing the neutralized prepolymer in water, and (3) chain
5 extending the neutralized, dispersed prepolymer by reaction with a primary
and/or secondary amine;

wherein a plasticizer is introduced into the reaction mixture as a diluent
at any time during prepolymer formation or before said prepolymer is dispersed
in water, and said plasticizer wholly or partially replaces other diluents or
10 solvents.

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ABSTRACT

Waterborne polyurethane dispersions are prepared by reacting (1) a polyisocyanate component; (2) an active hydrogen containing, high molecular weight component, such as a polyol or a polyamide; and (3) a water-solubilizing compound having water-solubilizing groups to form an isocyanate terminated prepolymer. The prepolymer subsequently is (1) neutralized by reaction with a tertiary amine, (2) dispersed in water, and then (3) chain extended by reaction with a primary and/or secondary amine. A plasticizer is introduced into the reaction mixture as a diluent at any time during prepolymer formation or before the prepolymer is dispersed in water. The plasticizer wholly or partially replaces other diluents or solvents.

The compositions prepared by the process of the present invention typically have lower modulus and higher solids than compositions of the prior art prepared using diluents such as N-methyl-2-pyrrolidone or solvents such as acetone, and are useful in applications such as surgical gloves. However, reaction components can be varied to include reactive plasticizers and other ingredients for preparation of harder materials useful in other articles, or to impregnate, saturate, spray or coat papers, non-woven materials, textiles, wood, metals, polymeric articles, and a variety of other substrates. Applications include gloves; papers and non-wovens; fibrous materials such as textiles;

4